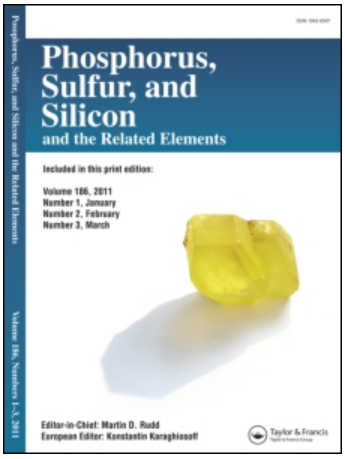

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Substituent Effects on the Stability of Sulfenes

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Substituent Effects on the Stability of Sulfenes

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The geometries and energies of substituted sulfenes RCH═SO_2 and alkenes RCH═CH_2 were calculated at the HF/6-311+G(2d,p) level. An isodesmic reaction was designed to study substituent effects on the stability of sulfenes. The correlation between substituent group electronegativity χ_{BE} and the stability of sulfenes was reasonably good. Electropositive and π-acceptor substituents stabilized sulfenes while electronegative substituents destabilized them.

Keywords Group electronegativity; Hartree-Fock (HF) calculations; isodesmic reactions; sulfenes

INTRODUCTION

Thiocarbonyl-S,S-dioxides, or sulfenes (**1**) (Scheme 1) are highly reactive molecules that may be considered sulfonyl analogs of ketenes or a derivative of sulfur trioxide. The first suggestion of a group of compounds called sulfenes was made by Wedekind and Schenk[1] and Staudinger and Pfeninger,[1,2] but their existence was proven by Opitz[3,4] and Bucher,[3] Opitz,[4] King et al., and King[6] using kinetic studies and trapping the reactive intermediates. Sulfines (**2**) (Scheme 2) are more stable at r.t. and can be studied directly using physical and chemical methods. Sulfenes are considerably less stable, and numerous attempts at their synthesis have failed; therefore, only indirect evidence about their existence and chemical properties is available. As a result, the comparative structural studies of sulfines and sulfenes have not been given much attention.

It has been suggested that sufficiently stabilized or sterically protected sulfenes could be isolated at r.t. and would exhibit the general properties of a sulfene, but so far all of these attempts have been unsuccessful. Attempts to obtain di-*tert*-butylsulfene (**3**) (Scheme 3) from different routes have been unsuccessful.[7,8]

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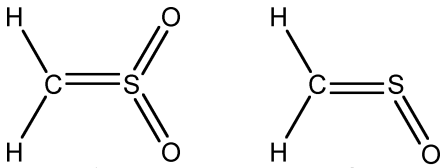
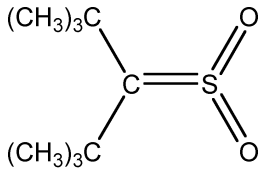


1 **2**

SCHEME 1



3

SCHEME 2

The direct observation of sulfenes using low-temperature matrix isolation techniques by King and Buchshriber[8] and Langendries et al.[9a] show spectroscopy evidence for their structure. Another direct observation of a sulfene has been described by Beck[9b] using a transient absorption with $\lambda_{max} = 315$ nm for the reaction of 2,5-dimethylphenylmethanesulfonyl chloride with triethylamine in aqueous THF. The signal, which appears after 50 ms and disappears after one second, was ascribed to 2,5-dimethylphenyl sulfene.[9b]

There are several reports regarding quantum mechanical calculations of sulfene using semiempirical methods, but in all of them a systematic study of substituents' effects on sulfene stability is missing.[10–13] Systematic studies of substituents' effects on molecules containing different functional groups have been presented in recent years. These studies involving ketenes,[14a–c] isocyanates,[14d] imines,[14d] allenes,[14c,15] ketenimines,[16a,b] carbodiimides,[16c] oxiranes,[16d] nitriles,[16e] isocyanides,[16e] cyclopropanes,[17] diazirines,[14c,18a,b] diazomethanes,[14c,18c–e] alkanes,[17] alkenes,[17a,c,19b] alkynes,[17a,b] 1,3-dienes,[20] cyclopropanes,[14a] carbonyl compounds,[19a,20b] carbocations,[21] carbanions,[22a] and organolithium compounds[22b] have been published in the literature.

In this article, we present a study on the influence of different substituents on the structure and stability of sulfenes using ab initio calculations and isodesmic reactions.

COMPUTATIONAL METHODS

All calculations reported here were performed with the *Gaussian 03* program.[23] All geometries were gradient optimized at the HF/6-311+G(2d,p) level. The orders (the number of negative diagonal elements of the Hessian matrix) of all critical points were evaluated at the same level to determine the nature of the located stationary points. Thus, all of the identified stationary points were properly characterized by an evaluation of the harmonic frequencies. This also provided the necessary thermodynamic data for the calculation of zero-point vibrational energies. To the best of our knowledge, there is no published scaling factor for this level of calculation; therefore, a scaling factor of 0.9 for zero-point vibrational energies was used with respect to the reported values for other levels in the literature.[14b,24]

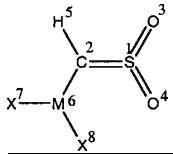
RESULTS

The selected optimized structural parameters, net atomic charges of sulfur and carbon of sulfenes **1–25**, and dipole moments calculated at HF/6-311+G(2d,p) level are given in Table 1.

The quantum mechanic calculations results indicate that all of the calculated sulfenes are planar and have a structure similar to alkenes. The parent sulfene (**1**) shows two identical S=O bond lengths of 1.404 Å and a C=S bond length of 1.562 Å with a C_{2v} point group. In all other substituted sulfenes, the two S=O bond lengths are not equivalent. Also, the two CSO bond angles are different in all substituted sulfenes.

The sulfene with a CH_3 substituent (**7**) shows a C=S bond length of 1.464 Å, which is slightly longer than the parent sulfene (**1**). The staggered conformation between the hydrogen of the sulfene and the CH_3 substituent was calculated as the stationary point, and the eclipsed conformation was calculated as the transition state. The sulfene with a SiH_3substituent (**14**) and the sulfene with a CF_3 substituent (**18**) have only the eclipsed conformation as the stationary point, and the staggered conformations were calculated as the transition state. In sulfenes **14** and **18**, the S=O bond lengths are 0.3 and 0.4 pm, respectively, which are longer than that in sulfene **1**. This trend was observed in sulfenes with the substituent group being BeH (**5a**), OH (**9**), F (**10**), Cl (**17**), and cyclopropyl (**24a**, **24b**), in which S=O bond lengths are 0.4 to 0.8 pm longer than the corresponding bond length in sulfene **1**. The sulfene with a BH_2 substituent (**6**) shows a bond length of 1.578 Å for the C=S bond, which is 2.5 pm longer than the corresponding bond in sulfene **1**. Similarly, sulfene with an AlH_2 substituent (**13a**) shows a bond length of 1.572 Å for the C=S bond, which is 1.0 pm longer than the C=S

TABLE I Calculated Bond Lengths (Å), Atomic Charges, Dipole Moments (D) of Sulfenes 1–25 and ΔE (kcal mol^{-1}) for the Isodesmic Reaction Shown in Eq. (1)

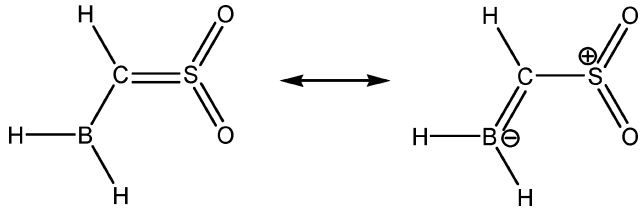


	R	Symmetry	χ_{BE}	r_{12}	S1	C2	μ(**D**)	ΔE
1	H	C_{2v}	2.20	1.562	1.28	1.23	1.23	0.00
5a	BeH	C_s	1.47	1.568	1.26	1.22	−0.42	−12.40
6	BH_2	C_s	1.93	1.587	−0.40	−0.29	−0.13	−7.64
7	CH_3	C_s	2.56	1.564	−0.15	3.22	2.95	0.63
8a	NH_2[a]	C_s	3.10	1.576	2.18	3.93	3.85	7.18
8b	NH_2	C_1	—	1.575	—	—	—	—
9	OH	C_s	3.64	1.568	1.22	1.22	1.35	11.64
10	F	C_s	4.00	1.568	1.28	1.20	−0.09	17.71
13a	AlH_2	C_s	1.62	1.572	0.03	−0.84	−0.63	−13.82
14	SiH_3	C_s	1.91	1.565	−0.35	2.43	2.58	−4.66
15a	PH_2[a]	C_s	2.17	1.570	2.99	3.10	3.52	−4.66
15b	PH_2	C_s	—	1.569	—	—	—	—
16	SH	C_1	2.63	1.574	1.22	1.24	1.36	4.59
17	Cl	C_s	3.05	1.567	1.31	1.31	−0.26	11.32
18	CF_3	C_s	2.68	1.566	−0.32	−0.32	−0.37	8.85
19	HC≡C	C_s	2.66	1.575	−0.27	2.79	2.44	3.76
20a	CHO[a]	C_s	2.60	1.576	1.99	2.77	0.72	2.78
20b	CHO	C_s	—	1.581	—	—	—	—
21a	H_2C=CH[a]	C_s	2.61	1.571	1.31	1.38	1.35	1.27
21b	H_2C=CH	C_s	—	1.571	—	—	—	—
22	NO_2	C_s	3.22	1.582	1.31	1.38	1.35	16.29
23	CN	C_s	2.69	1.577	1.31	1.38	1.35	7.70
24a	cyclopropyl[a]	C_s	2.56	1.565	1.31	1.38	1.35	1.13
24b	cyclopropyl	C_s	—	1.565	—	—	—	—
24c	cyclopropyl	C_1	—	1.568	—	—	—	—
25	Ph	C_s	2.58	1.570	1.31	1.38	1.35	1.29

[a]The most stable conformer

bond length in sulfene **1**. The longer bond length of sulfene **6** suggests a π-donation from the C=S bond, between the π orbital located on carbon and a empty coplanar 2p orbital of boron, as represented by the following resonance forms (Scheme 3).

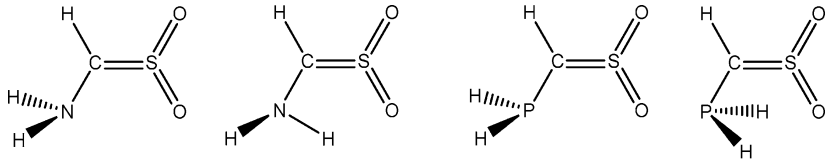
The 2p orbital of boron is closer in size and energy to 2p orbitals of carbon; therefore, this resonance form will be more important for boron than aluminum, and as a result, the C=S bond in sulfene **6** will be longer than the same bond in sulfene **13a**. Silicon is capable of having a similar type of π-donation, but because of the difference between the



SCHEME 3

3d orbitals of silicon and 2p orbitals of carbon, this effect is diminished, and the C═S bond length in sulfene **14** is almost the same length as the C═S bond in sulfene **7**.

The sulfene with a NH_2 group (**8**) (Scheme 4) has two stationary points, in which the structure of sulfene **8b** with C_1 symmetry is 1.2 kcal mol^{-1} more stable than sulfene **8a**, which has C_s symmetry. The sulfene with a PH_2substituent (**15**) (Scheme 4) also has two stationary points with C_s symmetry, and sulfene **15a** is 0.3 kcal mol^{-1} more stable than sulfene **15b**. The C═S bond in sulfene **15a** and sulfene **15b** are 1.570 Å and 1.569 Å, respectively, which are 0.7 and 0.5 pm shorter than the corresponding bond length in sulfene **8a**. This can be explained by the higher electronegativity of nitrogen, which pulls electrons from the C═S bond and increases the net charge on carbon when compared to phosphorus.

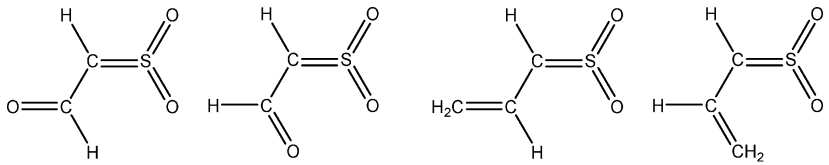


8a **8b** **15a** **15b**

SCHEME 4

For the elements of Group VI, the sulfene with an OH substituent (**9**) has only one stationary point. The C═S bond length in sulfene **9** is only 0.4 pm longer than the parent sulfene (**1**), and the negative net charge on carbon decreases from −0.42 in sulfene **1** to −0.09 in sulfene **9**. The sulfene with a SH substituent (**16**) also has onlyone stationary point in which the hydrogen of S-H is positioned out of the plane and is almost perpendicular to the plane of the sulfene. The C═S bond in sulfene **16** is 1.2 pm longer than the corresponding C═S bond in sulfene **1** and 0.6 pm longer than the corresponding C═S bond in sulfene **9**. The sulfene with an F substituent (**10**) and the sulfene with a Cl substituent (**17**) have slightly longer C═S bond lengths when compared to the corresponding bond length in sulfene **1**. These results suggest that

1. electronegative substituents, such as CF_3, OH, Cl, and F, cannot participate in resonance with the C=S bond, and this bond will be slightly longer than in the parent sulfene (**1**); and
2. electropositive substituents, such as BH_2 and AlH_2, are able to make the M=C bond by a π-donation from C=S to M and show a relatively longer C=S bond compared to sulfene **1**.



20a **20b** **21a** **21b**

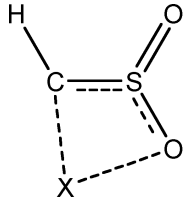
SCHEME 5

The sulfene with an acetylenic substituent (**19**) has only one stationary point with C_s symmetry, in which the C=S bond is 1.3 pm longer than the corresponding bond in sulfene **1**. The sulfene with a CH=O substituent (**20**) (Scheme 5) has two stationary points with C_s symmetry, in which sulfene **20a** with an s-*trans* conformation is 3.6 kcal mol^{-1} more stable than sulfene **20b**, which is the s-*cis* conformer. The C=S bond length in sulfene **20a** and sulfene **20b** are 1.576 Å and 1.581 Å, respectively, which are 1.4 pm and 1.9 pm longer than the corresponding bond in the parent sulfene (**1**). The sulfenewith a $CH{=}CH_2$ substituent (**21**) (Scheme 5) has both s-*trans* (**21a**) and s-*cis* (**21b**) stationary points, in which the s-*trans* is 2.9 kcal mol^{-1} more stable than the s-*cis* conformer. Both of these two conformations are completely planar with C_s symmetry. The C=S bond length of both conformers is calculated as 1.571Å, which is 0.9 pm longer than the C=S bond in sulfene **1**.

Sulfene **22** has only one stationary point in which the NO_2 group is in the same plane as the $C{=}SO_2$ fragment. The C=S bond length of sulfene **22** is 2.0 pm longer than that of sulfene **1**. Sulfene **23** also has one stationary point and a C=S bond length of 1.5 pm longer than C=S bond of sulfene **1**. The sulfene with a cyclopropyl substituent (**24**) has three stationary points in which sulfene **24a** with a C_s symmetry is calculated as 0.8 kcal mol^{-1} more stable than sulfene **24b** and 2.8 kcal mol^{-1} more stable than **24c**. The C=S bond lengths in sulfene **24** are 0.3 to 0.6 pm longer than in the parent sulfene (**1**). The sulfene with a phenyl substituent (**25**) shows only one stationary point with C_s symmetry, in which the phenyl ring is coplanar with the sulfene $C{=}SO_2$

fragment. The C=S bond length in sulfene **25** is 0.8 pm longer than the corresponding bond in sulfene **1**.

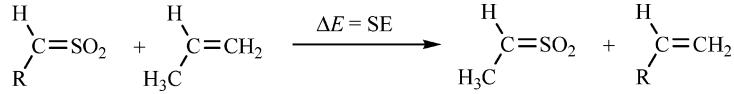
Sulfenes with electropositive substituents, such as Na, Li, BeH, MgH, BeH_2, and AlH_2, show unusual bridged structures. The carbon of sulfene shows some negative-charge character (Table 1) and, along with the oxygen atoms, are able to coordinate to the electropositive atoms (Scheme 6). This type of bridged structure has been found by computational and experimental studies for other functional groups.[14c,16a,16c,25] Because of the unique structure of the previously discussed sulfenes with electropositive substituents, they were excluded from the list of substituents used for isodesmic energy calculations.



4 X = Li
5b X= BeH
11 X= Na
12 X= MgH
13b X= AlH_2

SCHEME 6

Isodesmic and homodesmic reactions are suitable to predict the stability of compounds because systematic errors in the energy of reactants and productscan be canceled out. A simple computational approach can be used to estimate the heats of reaction.[24,26] In general, a substituted product of onetype is more stable than the substituted reactants of another type if the isodesmic or homodesmic reaction is exothermic, and a substituted reactant of one type is more stable than the substituted reactants of another type if the reaction is endothermic. Therefore, the isodesmic methyl exchange reaction between propene and a substituted sulfene (Eq. (1)) was used to study the stabilization effects of a substituent R on a sulfene when compared to an alkene:



(1)

In this reaction, the number of C=C, C=S, S=O, C-R, and C-H bonds are unchanged, and R is transferred from one sp^2 planar carbon to another; therefore, the energy change resulting from factors other than the electronic stabilization are minimized. The calculated energies at the HF/6-311+G(2d,p) level were used to calculate the isodesmic stabilization energies (Eq. (1)) and are given in Table 1.

Several different electronegativity scales have been reported in the literature.[27] It has been shown that for cumulene systems, such as

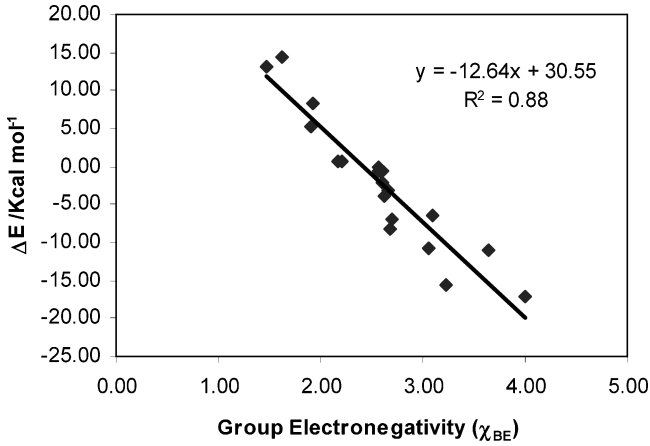


FIGURE 1 A plot of ΔE of the isodesmic reaction (Eq. (1)) against substituted group electronegativity (χ_{BE}).

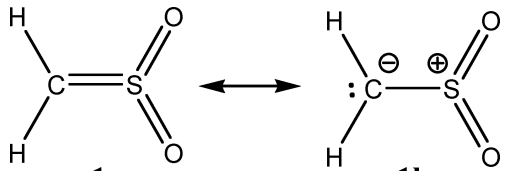
ketenes, ketenimines, allenes, isocyanates, diazomethanes, and carbodiimides, the Boyd and Edgecomb scale[27b] gives the best correlation of substituent effects. The χ_{BE} values are available for many different substituents, and we have chosen the substituents with available group electronegativities. Because the electronegativity of hydrogen is not available in the Boyd and Edgecomb scale, the Pauling value of 2.0 was used. A plot of the ΔE values for the isodesmic reaction against the substituent group electronegativity (Figure 1) gives a linear correlation ($r^2 = 0.88$) as represented by Eq.(2):

$$\Delta E = -12.64\chi_{BE} + 30.55 \quad (2)$$

The negative slope of Eq. (2) indicates that the stabilization energy of the isodesmic reaction (Eq. (1)) decreases as the electronegativity of the substituent increases. Electronegative substituents, such as F, Cl, OH, and NO_2, show significant negative stabilization energies, while electropositive substituents, such as BeH, AlH_2, and SiH_3, show positive stabilization energies. Eq. (2) shows a relatively good correlation between the stabilization energy (Eq.(1), $\Delta E = \mathrm{SE}$) and group electronegativity of different substituents. This correlation indicates that substituents, such as F, Cl, OH, NO_2, and CF_3, destabilize the sulfenes, while electropositive groups, such as BH, MgH, BeH_2, and SiH_3, stabilize them. The same type of studies for ketenes,[14a–c] allenes,[14c,15] diazomethane,[14c,18c–e] isocyanates,[14d] carbodiimides,[16c] and ketenimines[16] show a negative slope to the correlation curve, meaning the previously discussed functional groups are stabilized by electropositive substituents. The absolute values of the slopes of correlation

curves are 15.6 for ketenes, 5.8 for allenes, 10.6 for diazomethanes, 23.6 for isocyanates, 16.5 for carbodiimides, 11.3 for ketenimines, and 12.6 for sulfenes. These numbers indicate that among these functional groups, isocyanates are most sensitive to substituent group electronegativity, and sulfenes show moderate sensitivity to this. The order of sensitivity to substituent group electronegativity is isocyanates > carbodiimides > ketenes > sulfenes > ketenimines > diazomethanes > allenes. This order implies that the electronegative heteroatom at the two ends of these groups may produce a higher sensitivity of functional group stability to substituents via a larger dipole in the functional group and other electronic effects.

In all of the calculations, the sulfene moiety shows planarity, and the nature of the substituent has no effect on that. This indicates that the most stable conformation of sulfenes is planar with ionic character. These calculations also show a negative charge on the oxygen and the carbon atoms, and a positive charge on the sulfur atom, which is consistent with the expected resonance forms of sulfene **1b** (Scheme 7). Because the carbon sulfenes carries a negative charge, we expect that π-acceptor substituents, such as BeH, BH_2, AlH_2, and SiH_3, can stabilize the negative charge, which is supported by the isodesmic reaction stability energies as well.



1a **1b**

SCHEME 7

Substituents, such as CN, CHO, C≡C, NO_2, and Ph (which have unsaturated bonds conjugated with sulfenes and serve as π-acceptors), are able to delocalize the π electrons of sulfenes and stabilize them. In the case of NO_2, the large electronegativity ($\chi_{BE} = 3.22$) overcomes the π-acceptance ability and destabilize the sulfene.

CONCLUSION

The stability of sulfenes is dependent on the nature of the substituents as well as their group electronegativity. Generally, electronegative substituents destabilize sulfenes, while electropositive substituents stabilize them. In comparison to other studied functional groups, sulfenes are less sensitive to substituent group electronegativity than isocyanates, carbodiimides, and ketenes, but they are more sensitive than

ketenimines, diazomethanes, and allenes. The conjugation of π-acceptance substituents with sulfene gives extra stability to them. In all calculations, the sulfene moiety has a planar structure with a large dipole moment on the C=S bond. These calculations suggest that only sulfenes with π-acceptor substituents could be stable, and the synthesis and isolation of sulfenes must be focused on these substituents.

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